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Research Paper

Enhanced electrocatalytic activity and durability of Pt nanoparticles decorated on GO-PVP hybriide material for methanol oxidation reaction



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ABSTRACT

The alternative energy request is force to find effective electro catalysts used in fuel cell implementations and to enhance the efficiency of existing materials. In this study, graphene oxide (GO) and polyvinylpyrrolidone (PVP) supported shape-controlled platinum nanoparticles (Pt NPs) were newly synthesized with one-pot approach and used as anode materials in the direct methanol fuel cells (DMFCs). The examination for the performance of Pt @GO-PVP NPs was carried out in methanol oxidation reactions (MOR). Pt @GO-PVP catalysts exhibit high stability and activity against the MOR. The methanol oxidation reactions current can reach to 43 mA and can maintain 82.9% of the initial value even after 1000 cycles. The GO-PVP support material provides higher surface area and absorbs more methanol molecules for more efficient oxidation.

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1. Introduction

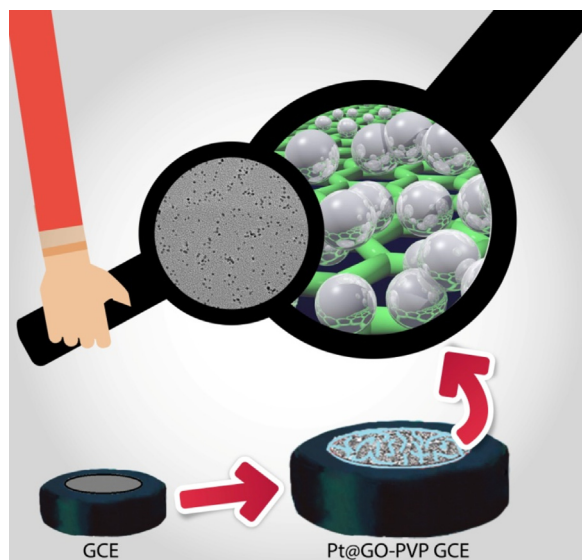
Energy consumption is increasing rapidly due to population growth, industrialization and technological development. In addition to rising energy demand, fossil energy reserves are also rapidly declining. However, the deterioration of the natural environment is another threat. Nowadays, renewable and environmentally friendly sources such as fuel cells are receiving attention, instead of fossil energy sources that are decreasing their reserves [1–9]. Methanol performs better than gasoline and diesel because of its safe, high energy efficiency, ease of use and low carbon emissions. Among different types of fuel cells, direct methanol fuel cells (DMFC) are considered as a highly promising future power source due to their low pollutant emission, high energy density and economy [10–15]. Despite great effort in the development of DMFCs, there are obstacles that restrict the commercialization of DMFCs. There are two basic obstructions: low activity and high price. Recent studies show that Pt metal has the superior catalytic activity and long-term operation stability for methanol oxidation and they are synthesized using different supporting materials to prevent rapid deactivation of catalysts and increase stability [16–23]. The interaction between the catalyst and the support not only increases the

catalyst activity but also reduces catalyst loss and price. Supporting materials also helps to improve catalyst performance and durability by reducing catalyst poisoning. For this purpose, among the supporting materials, graphene has great predominance because of its great conductivity, low cost, large surface area, high elasticity and stable electrochemical properties. Besides graphene oxide, PVP is also supposed to be the new supporting material due to its chemical stability, nontoxicity and excellent solubility in many polar solvents [24–29]. It is contemplated that the use of GO and PVP hybriide together as catalyst support may improve the electrochemical activity of the catalysts. For this purpose, Pt nanoparticles will be placed on the carbon-polymer support (GO-PVP) material to make the Pt catalysts more economical and effective for MOR. Generally, MOR proceeds slowly because a lot of paths are required to convert methanol to CO₂ via a few electron transfers. Furthermore, CO intermediates will be released due to unfinished oxidation of methanol [33–43]. CO intermediates will be adsorbed to the Pt surface, thereby rapidly inactivating the Pt catalysts. In order to eliminate this case, Pt nanoparticles were deposited on graphene oxides with the presence of polyvinylpyrrolidone (PVP) which were synthesized by one pot method (Pt@GO-PVP). GO and PVP hybriide serve as a supporting material and stabilizer. Curiously, these Pt@GO-PVP nanomaterials show a high catalytic activity and long term stability on MOR. Thus this work will be helpful for the challenges of commercialization of DMFCs.

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Scheme 1. Schematic illustration of Pt@GO-PVP NPs.

2. Material and methods

2.1. Synthesis of Pt@GO-PVP NPs nanocomposite

Graphene oxide (GO) was synthesized by modified Hummers method from graphite [See Supporting info]. To synthesize the new Pt@GO-PVP hybrid nanocomposite catalyst; First, 30 mg of PVP was mixed in 30 mL of distilled water for 1 h to homogeneously disperse in an ultrasonic bath. Then, 30 mg of graphene oxide (GO) and 30 mL of distilled water were added and stirring was continued for 1 h. After mixing, 2 mL (0.01 M) of PtCl_4 salt was added to the mixture and the mixture was allowed to stir for another 30 min and the reducing agent, DMAB (148 mg) was added and stirred in the ultrasonic bath. After the sonication process Pt@GO-PVP nanocatalyst was obtained. This nanocatalyst was washed with a pure water-ethanol mixture to remove the excess GO and/or PVP and then left to dry under vacuum. The same processes used in the synthesis of Pt@GO-PVP nanocatalyst were also used for the comparison of Pt@GO and Pt@PVP catalysts for comparison (Scheme 1).

3. Results and discussion

Pt@GO, Pt@PVP and Pt@GO-PVP nanoparticles were prepared by in-situ one pot method and their characterizations were performed by SEM, TEM, XRD, RAMAN and XPS techniques. Surface morphologies and structures of Pt@GO NPs, Pt@PVP NPs and Pt@GO-PVP NPs nanocomposites were characterized by TEM and HRTEM. Pt nanoparticles were distributed on GO-PVP hybrid material which were in the form of black spots and indicated in Fig. 1a. The average size of the Pt@GO-PVP nanoparticles was found to be 3.89 nm (Fig. 1) in the HRTEM analysis. The atomic lattice fringes obtained from HRTEM were also shown in Fig. 1b. The HRTEM image shows a plane with 0.23 nm lattice fringe, suggesting that Pt nanoparticles were in face-centered cubic (fcc) (111) structure. Fig. 1c also shows the representative scanning electron microscopy (SEM) image of Pt@GO-PVP nanoparticles. It appears that the Pt nanoparticles are very good distributed on the GO-PVP hybrid material and there is not much agglomeration in prepared nanomaterials.

The crystal structure of all prepared catalysts was analyzed using by XRD and typical peaks are shown in Fig. 2a. The XRD pattern peaks at about $2\theta = 39.83^\circ$, 46.70° , 67.82° , 81.30° and 86.15° that are related to the Pt (111), (200), (220), (311) and (222) planes. At the same time, strong diffraction Pt (111) facet is seen

at 39.83° . These characteristic diffraction peaks show that Pt is a face-centered cubic structure in all catalysts. Furthermore, Scherrer Formula was used to calculate the Pt particle size [25]. The average particle size for Pt@GO-PVP NPs was found to be 3.81 nm and the particle sizes of all nanoparticles are summarized in Table S1.

Raman spectroscopy is also a powerful and effective technique to understand the structural features, composition and the ordered and disordered crystal structure of carbon in carbonaceous materials [44–47]. Raman spectroscopic analysis was performed for GO and Pt@GO-PVP as shown in Fig. 2b in detail. According to Raman spectrum, the GO and Pt@GO-PVP exhibit two remarkable scattering peaks centered at 1351.5 cm^{-1} and 1587.8 cm^{-1} corresponding to the D-band (E_{2g} phonon of sp^2 carbon atoms) and G-band (breathing mode of A_{1g} symmetry), respectively. The ratios of the intensities of the D band and the G band for GO and Pt@GO-PVP are 1.00 and 1.30 respectively. The increased D peak of Pt@GO-PVP indicates the functionalization of GO with PVP and Pt.

X-ray photoelectron spectroscopy (XPS) was also used to investigate the oxidation states of the synthesized catalysts. The Pt 4f region of the spectrum was analyzed in Pt@GO NPs (Fig. 3a), Pt@PVP NPs (Fig. 3b) and Pt@GO-PVP NPs (Fig. 3c) in order to see the platinum surface oxidation state (Fig. S2). The subtraction of the Shirley-shaped background and fittings of XPS peaks were exerted by Gaussian–Lorentzian method. After smoothing, the relative intensities of the species were measured by calculating the integral of each peak. The more dense peaks in the Pt 4f spectrum correspond to the zero-valued platinum, which is observed at about 71.2–71.6 and 74.4–74.7. Other doublets are associated with unreduced Pt derivatives and occur at higher binding energies. The unreduced Pt derivatives correspond to Pt(II) and/or Pt(IV). These doublets are seen at about 72.4–74.7 and 75.6–77.9 eV. When the relative peak areas are examined, a large part of the surface atoms of Pt nanoparticles were not oxidized and the percentage of Pt (0) species was found to be about $\geq 80\%$. Besides, Fig. S1(a) shows C 1s core level XPS spectra of GO-PVP hybrids. A peak is located 284.6 eV in the C1s spectrum attributed to the sp^2 -hybridized carbon of graphite. The carbon backbone of the GO-PVP hybrid is also active in the presence of this peak. Species with binding energies at about 286.6, 287.9 and 290.1 eV are related with the presence of C–N, C–OH and C=O and these may be connected with environment and adsorbed oxygenated species. The O1s core level peak at 530.4 eV is called linkage oxygen. Apart from this, there are terminal oxygen at 530.4 eV and a peak at 531.6 eV which is supposed to result from humidity in ambient.

After the fully characterization of all prepared catalysts, the cyclic voltammogram (CV) measurements of Pt@GO NPs, Pt@PVP NPs and Pt@GO-PVP NPs catalysts were carried out in the absence of methanol as blank CVs in N_2 -saturated 0.5 M H_2SO_4 solution (Fig. S3). Hydrogen adsorption and desorption regions in nanocatalysts correspond to -0.2 to 0 V which represent the electrochemical surface area (ECSA) of the nanocatalysts. The hydrogen area in the CV curve was used to calculate the ECSA and was obtained from the following formula [25]:

$$\text{ECSA} = \frac{Q \text{ (mC)}}{[\text{Pt}] \times 0.21 \text{ mC/cm}^2}$$

where [Pt] represents the platinum content or loading in the electrode, Q is the charge density for hydrogen desorption and 0.21 (mC/cm^2) represent the charge required to oxidize a monolayer of protons on Pt. The chemical surface areas (CSA) of the prepared catalysts were calculated using the Saurer Formula [25]:

$$\text{CSA} = \frac{6 \times 10^3}{\rho \times d}$$

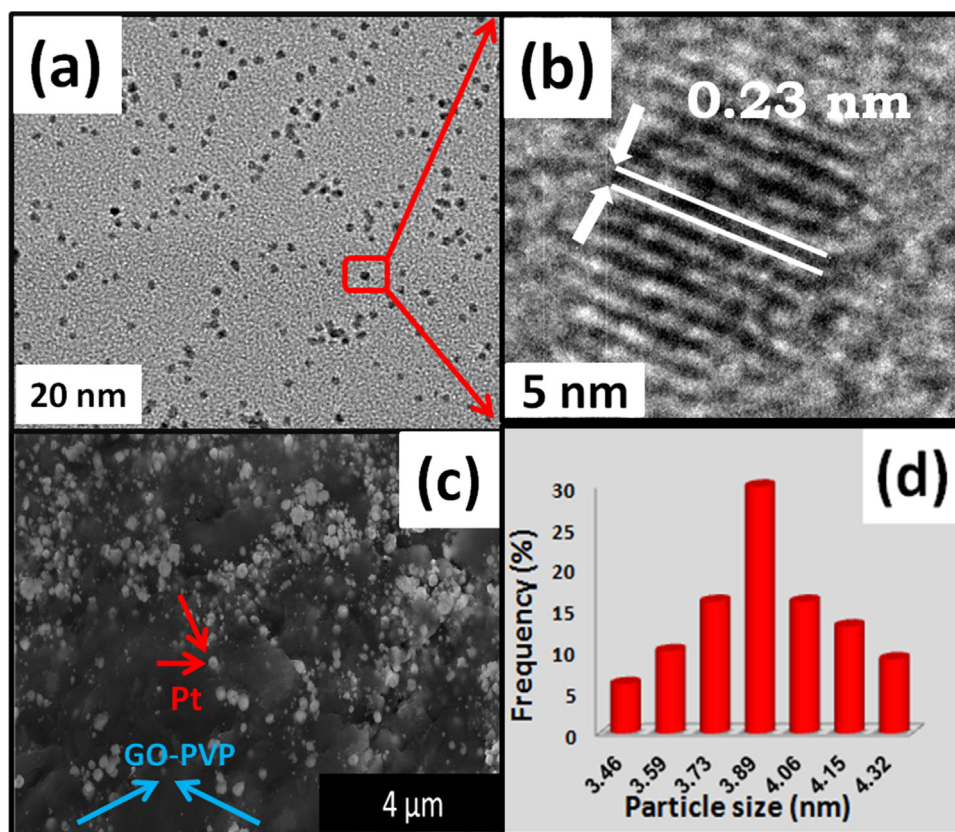


Fig. 1. TEM image (a), HRTEM image (b) SEM image (c) and the particle size histogram (d) of Pt@GO-PVP NPs.

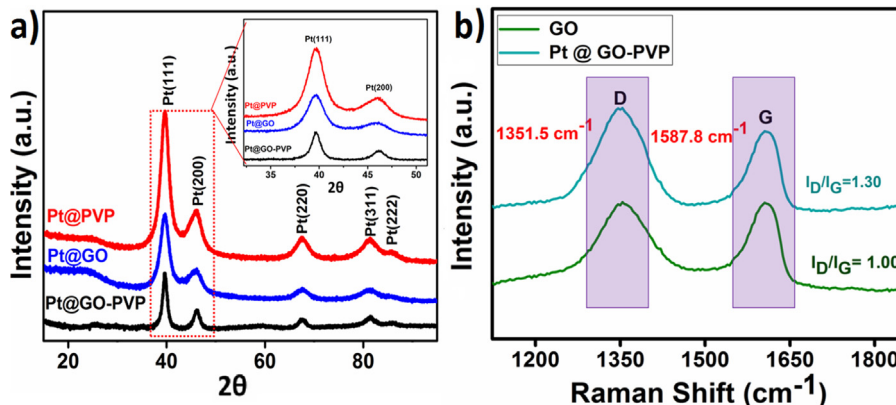


Fig. 2. XRD patterns of Pt@GO-PVP NPs, Pt@GO NPs and Pt@PVP NPs (a), Raman spectra of GO and Pt@GO-PVP (b).

where d is the average Pt particle size in nm (from XRD measurements) and q is the density of Pt metal (21.4 g/cm^3). The Pt utilization value of the Pt catalysts is defined as follows [30–32]:

$$\text{Utilization (\%)} = \frac{\text{ECSA}}{\text{CSA}} \times 100$$

ECSA, CSA and % Pt utility values of the catalysts are given in Table S1. When the obtained values are examined, it can be concluded that Pt@GO-PVP NPs have higher Pt utility value and active surface area than the other prepared catalysts. The electrocatalytic activity of the prepared catalysts towards methanol oxidation is investigated in Fig. 4. (in N_2 saturated $0.5 \text{ M H}_2\text{SO}_4$ solution containing $0.5 \text{ M CH}_3\text{OH}$). It was observed that there were two distinct oxidation peaks in the forward and backward potential scans. As can be seen, the main oxidation peak of methanol in Pt @ GO-PVP

NPs is about 0.38 V potential in forward scan and the peak current density at the same potential is 43 mA . The oxidation current on Pt@GO-PVP NPs is significantly decreased at about 0.59 V due to the formation of Pt oxides. Due to the removal of the oxidized carbonaceous species formed during the forward scan and the electro oxidation of the methanol, the main oxidation peak in the backward scan is at about 0.05 V . When the electro catalytic performances of the prepared catalysts are compared Pt @ GO-PVP NPs were found to be approximately 1.53 and 2.87 times more active than Pt@PVP NPs and Pt@GO NPs, respectively. More active sites can be occurred with GO-PVP composites and thanks to these active sites, more alcohol can be adsorbed on the surface of the Pt @ GO-PVP catalyst for methanol oxidation.

It has been also observed that when the PVP are combined with the GO in the direction of the obtained results, the activities against

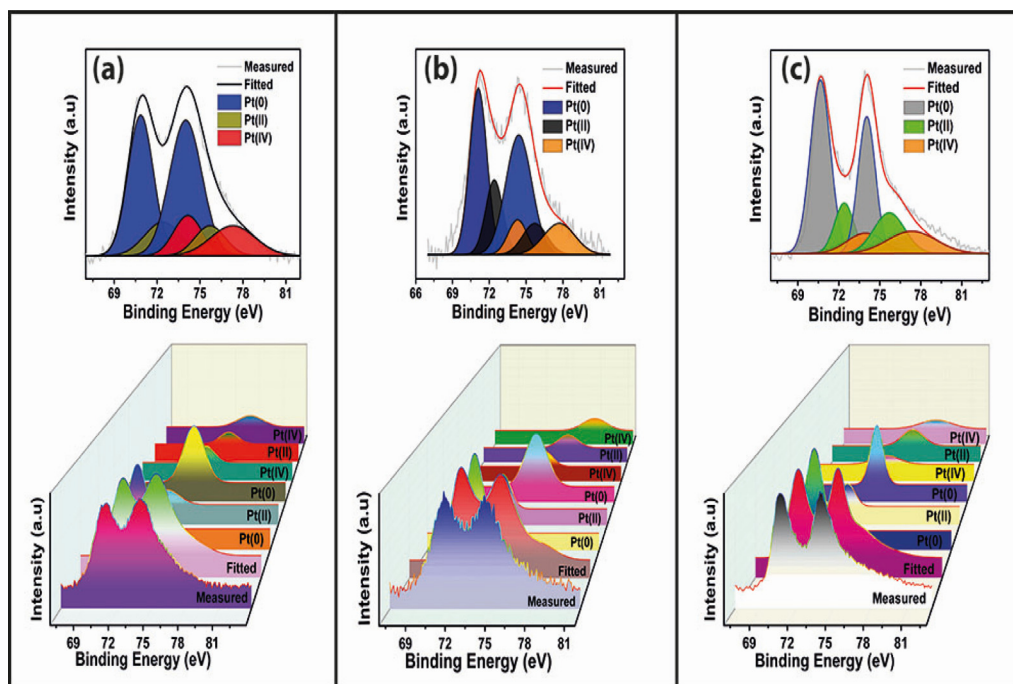


Fig. 3. The Pt 4f XPS spectra of Pt@GO NPs (a), Pt@PVP NPs (b) and Pt@GO-PVP NPs (c).

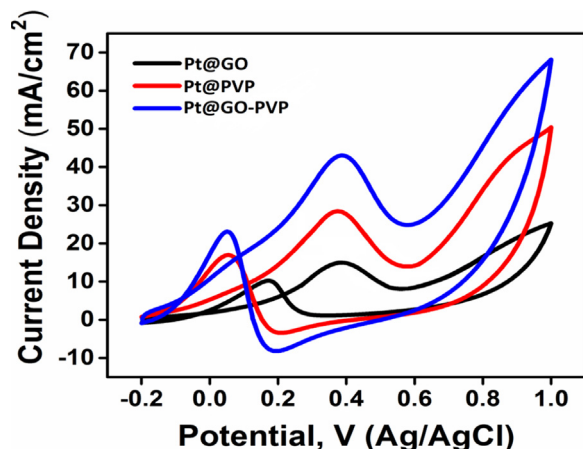


Fig. 4. Cyclic voltammograms of Pt@GO NPs, Pt@PVP NPs and Pt@GO-PVP NPs in nitrogen saturated solution of 0.5 M H_2SO_4 containing 0.5 M CH_3OH at a scan rate of 50 mV s^{-1} .

alcohol have great efficiency. The way in which hybrid structures (GO-PVP) altered activity and stability was examined in this way. The adsorption rate of the methanol molecule was also increased by increasing the active surface area with GO-PVP hybrid support. The use of the hybrid support prevented the electrocatalytic reduction in the methanol oxidation reaction, and the resulting catalytic activity was much higher than that of the individual metal-polymer or metal-carbon catalysts. After obtaining the highest anodic peak potential, chronoamperometry (CA) was also used for the stability tests of the prepared catalysts and the currents between the 1st and 1000th cycles were compared for the long-term stability test using by cyclic voltammetry. As can be seen in Fig. S4, GO-PVP supported Pt nanoparticles have better catalytic activity even after 1000 cycles compared to other catalysts due to unique *p*-conjugate structures. In addition, the GO-PVP composite has good stability and excellent electrical conductivity in acidic environments. Representative CA curves obtained for 1000 s at 0.39 V potential for methanol oxidation are shown in Fig. 5. It is understood that GO-PVP supported Pt

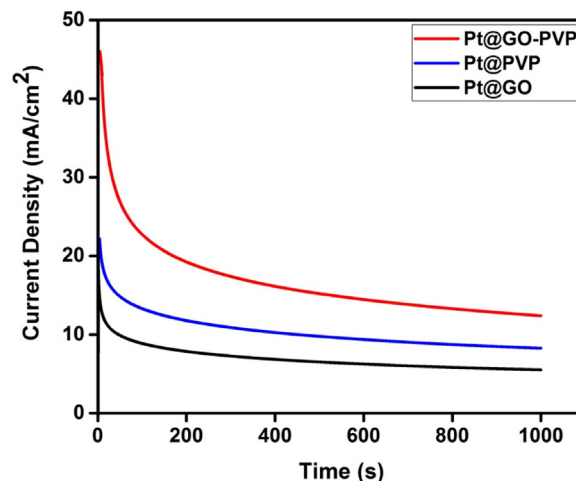


Fig. 5. Chronoamperometry voltammograms of Pt@GO NPs, Pt@PVP NPs and Pt@GO-PVP NPs in nitrogen saturated solution of 0.5 M H_2SO_4 containing 0.5 M CH_3OH at the potential of 0.39 V, respectively.

nanoparticles have higher catalytic efficiency and durability than the other catalyst when compared current after 1000 s. Oxidation currents rapidly declined at the early phase of the chronoamperometric measurements. The significant drop of the current is mainly due to the following reasons. At the beginning of the potential scan, a rapid accumulation of strongly adsorbed species (CO, oxyanion etc.) occurred on the electron surface, which causes the number of active sites to decrease rapidly. Besides, there would be an electric-double layer charge process at the electrolyte/catalyst interface. These results show us that the electrochemical activity against for methanol oxidation is much higher when the Pt@ GO-PVP hybrid nanocatalyst is supported on both GO and PVP, and it is important for researchers to synthesize more stable and more effective new nanocomposites. Nanocatalysts such as Pt@ GO-PVP, which have superior properties in this way; are very promising in the near future for fuel cells and capacitors.

4. Conclusions

In summary, GO, PVP and GO-PVP composite supported Pt nanocatalysts were synthesized by in-situ one step method. Synthesis was performed in one step using an eco-friendly methodology in which combination of sonochemical and DMAB reduction methods. Pt@GO-PVP NPs exhibit exceptional performance as a catalyst for the electro oxidation of methanol compared to Pt@GO NPs and Pt @PVP NPs due to higher active sites and high amount of Pt(0). The GO-PVP nanocomposite provides a large surface area for the activity of the Pt nanoparticles. At the same time, the synergistic effect of the composites with Pt nanoparticles significantly increased the catalytic activity. This controllable and easy method offers a new way to prepare new nanocatalysts with high catalytic activity. Comprehensive applications can be achieved in direct methanol fuel cells using catalysts synthesized by this method.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.08.014>.

References

- [1] Z. Qi, A. Kaufman, Performance of 2-propanol in direct-oxidation fuel cells, *J. Power Sources* 112 (2002) 121–129.
- [2] I. Dincer, Hydrogen and fuel cell technologies for sustainable future, *Jordan J. Mech. Ind. Eng.* 2 (2008) 1–14.
- [3] D. Cao, S.H. Bergens, A direct 2-propanol polymer electrolyte fuel cell, *J. Power Sources* 124 (2003) 12–17.
- [4] (a) Y. Yıldız, H. Pamuk, O. Karatepe, Z. Dasdelen, F. Sen, Carbon black hybrid material furnished monodisperse platinum nanoparticles as highly efficient and reusable electrocatalysts for formic acid electro-oxidation, *RSC Adv.* 6 (2016) 32858–32862; (b) H. Pamuk, B. Aday, F. Sen, M. Kaya, Pt NPs@GO as a highly efficient and reusable catalyst for one-pot synthesis of acridinedione derivatives, *RSC Adv.* 5 (2015) 49295–49300; (c) E. Erken, I. Esirden, M. Kaya, F. Sen, A rapid and novel method for the synthesis of 5-substituted 1H-tetrazole catalyzed by exceptional reusable monodisperse Pt NPs@AC under the microwave irradiation, *RSC Adv.* 5 (2015) 68558–68564.
- [5] H. Uchida, Y. Mizuno, M. Watanabe, Suppression of methanol crossover and distribution of ohmic resistance in Pt-dispersed PEMs under DMFC operation: experimental analyses, *J. Electrochem. Soc.* 149 (2002) A682–A687.
- [6] L.F. Dong, R.R.S. Gari, Z. Li, M.M. Craig, S.F. Hou, Graphene-supported platinum and platinum-ruthenium nanoparticles with high electrocatalytic activity for methanol and ethanol oxidation, *Carbon* 48 (2010) 781–787.
- [7] Z. Qi, M. Hollett, A. Attia, A. Kaufman, Low temperature direct 2-propanol fuel cells, *Electrochem. Solid State Lett.* 5 (2002) A129–A130.
- [8] S. Liao, K.A. Holmes, H. Tsapraillis, V.I. Birss, High performance PtRu catalysts supported on carbon nanotubes for the anodic oxidation of methanol, *J. Am. Chem. Soc.* 128 (2006) 3504–3505.
- [9] P. Bera, K.R. Priolkar, A. Gayen, P.R. Sarode, M.S. Hegde, S. Emura, R. Kumashiro, V. Jayaram, G.N. Subbanna, Ionic dispersion of Pt over CeO₂ by the combustion method: structural investigation by XRD, TEM, XPS, and EXAFS, *Chem. Mater.* 15 (2003) 2049–2060.
- [10] (a) F. Sen, G. Gokagac, Improving catalytic efficiency in the methanol oxidation reaction by inserting Ru in face-centered cubic Pt nanoparticles prepared by a new surfactant, *tert*-octanethiol, *Energy Fuels* 22 (2008) 1858–1864; (b) F. Ozturk, S. Sen, G. Gokagac, The preparation and characterization of nano-sized Pt-Pd alloy catalysts and comparison of their superior catalytic activities for methanol and ethanol oxidation, *J. Mater. Sci.* 47 (2012) 8134–8144; (c) S. Celik, E. Kuzu, H. Erken, Y. Koskun, F. Sen, Nearly monodisperse carbon nanotube furnished nanocatalysts as highly efficient and reusable catalyst for dehydrocoupling of DMAB and C1 to C3 alcohol oxidation, *Int. J. Hydrogen Energy* 41 (2016) 3093–3101.
- [11] Y. Ko, J. Kim, D. Kim, Y. Yamauchi, J.H. Kim, J. You, A simple silver nanowire patterning method based on poly(ethylene glycol) photolithography and its application for soft electronics, *Sci. Rep.* 7 (2017) 2282, <http://dx.doi.org/10.1038/s41598-017-02511-8>.
- [12] W.C. Choi, J.D. Kim, S.I. Woo, Quaternary Pt-based electrocatalyst for methanol oxidation by combinatorial electrochemistry, *Catal. Today* 74 (2002) 235–240.
- [13] Z. Rong, Z. Sun, Y. Wang, J. Lv, Y. Wang, Selective hydrogenation of cinnamaldehyde to cinnamyl alcohol over graphene supported Pt-Co bimetallic catalysts, *Catal. Lett.* 144 (6) (2014) 980–986, <http://dx.doi.org/10.1007/s10562-014-1209-5>.
- [14] Y.B. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature* 438 (2005) 201–204.
- [15] J. Liu, T. Zhao, Z. Liang, R. Chen, Effect of membrane thickness on the performance and efficiency of passive direct methanol fuel cells, *J. Power Sources* 153 (2006) 61–67.
- [16] Y. Hao, X. Wang, J. Shen, J. Yuan, A. Wang, L. Niu, S. Huang, One-pot synthesis of single-crystal Pt nanoplates uniformly deposited on reduced graphene oxide, and their high activity and stability on the electrocatalytic oxidation of methanol, *Nanotechnology* 27 (2016) 145602.
- [17] J. Kim, J. Lee, J. You, M.-S. Park, M.S.A. Hossain, Y. Yamauchi, J.H. Kim, Conductive polymers for next-generation energy storage systems: recent progress and new functions, *Mater. Horiz.* 3 (2016) 517–535.
- [18] G. Andreadis, P. Tsiakaras, Ethanol crossover and direct ethanol PEM fuel cell performance modelling and experimental validation, *Chem. Eng. Sci.* 61 (2006) 7497–7508.
- [19] M. Ahmed, I. Dincer, A review on methanol crossover in direct methanol fuel cells: challenges and achievements, *Int. J. Energy Res.* 35 (2011) 1213–1228.
- [20] Y. Devrim, S. Erkan, N. Bac, I. Eroglu, Improvement of PEMFC performance with Nafion/inorganic nanocomposite membrane electrode assembly prepared by ultrasonic coating technique, *Int. J. Hydrogen Energy* 37 (2012) 16748–16758.
- [21] H. Uchida, K. Izumi, M. Watanabe, Temperature dependence of CO-tolerant hydrogen oxidation reaction activity at Pt, Pt-Co, and Pt-Ru electrodes, *J. Phys. Chem. B* 110 (2006) 21924.
- [22] H. Tan, Y. Li, X. Jiang, J. Tang, Z. Wang, H. Qian, P. Meia, V. Malgras, Y. Bando, Y. Yamauchi, Perfectly ordered mesoporous iron-nitrogen doped carbon as highly efficient catalyst for oxygen reduction reaction in both alkaline and acidic electrolytes, *Nano Energy* 36 (2017) 286–294.
- [23] H. Shin, K.K. Kim, A. Benayad, S. Yoon, H.K. Park, I. Jung, M.H. Jin, H. Jeong, J.M. Kim, J. Choi, Y.H. Lee, Efficient reduction of graphite oxide by sodium borohydride and its effect on electrical conductance, *Adv. Funct. Mater.* 19 (2009) 1987.
- [24] J. Zhang, Y. Tang, C. Song, H. Wang, PEM fuel cell open circuit voltage (OCV) in the temperature range of 23 °C to 120 °C, *J. Power Sources* 163 (2006) 532–537.
- [25] (a) O. Karatepe, Y. Yıldız, H. Pamuk, S. Eris, Z. Dasdelen, F. Sen, Enhanced electrocatalytic activity and durability of highly monodisperse Pt@PPy-PANI nanocomposites as a novel catalyst for the electro-oxidation of methanol, *RSC Adv.* 6 (2016) 50851; (b) Y. Yıldız, İ. Esirden, E. Erken, E. Demir, M. Kaya, F. Sen, Microwave (Mw)-assisted synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition catalyzed by Mw-Pd/Co nanoparticles decorated on multi-walled carbon nanotubes, *ChemistrySelect* 8 (2016) 1695–1701; (c) B. Celik, G. Baskaya, H. Sert, O. Karatepe, E. Erken, F. Sen, Monodisperse Pt(0)/DPA@GO nanoparticles as highly active catalysts for alcohol oxidation and dehydrogenation of DMAB, *Int. J. Hydrogen Energy* 41 (2016) 5661–5669.
- [26] R.D. Heidenreich, W.M. Hess, L.L. Ban, A test object and criteria for high resolution electron microscopy, *J. Appl. Crystallogr.* 1 (1968) 1–8.
- [27] M.I. Katsnelson, K.S. Novoselov, A.K. Geim, Chiral tunnelling and the Klein paradox in graphene, *Nat. Phys.* 2 (2006) 620–625.
- [28] Y. Gao, P. Jiang, D.F. Liu, H.J. Yuan, X.Q. Yan, Z.P. Zhou, J.X. Wang, L. Song, L.F. Liu, W.Y. Zhou, G. Wang, C.Y. Wang, S.S. Xie, Evidence for the monolayer assembly of poly(vinylpyrrolidone) on the surfaces of silver nanowires, *J. Phys. Chem. B* 108 (2004) 12877–12881.
- [29] K.M. Koczkur, S. Mourdikoudis, L. Polavarapu, S.E. Skrabalak, Polyvinylpyrrolidone (PVP) in nanoparticle synthesis, *Dalton Trans.* 44 (2015) 17883–17905.
- [30] R.C. Merrifield, Z.W. Wang, R.E. Palmer, J.R. Lead, Synthesis and characterization of polyvinylpyrrolidone coated cerium oxide nanoparticles, *Environ. Sci. Technol.* 47 (2013) 12426–12433.
- [31] M.M. Liu, R.Z. Zhang, W. Chen, Graphene-supported nanoelectrocatalysts for fuel cells: synthesis, properties, and applications, *Chem. Rev.* 114 (2014) 5117–5160.
- [32] (a) E. Erken, H. Pamuk, O. Karatepe, G. Baskaya, H. Sert, O.M. Kalfa, F. Sen, New Pt(0) nanoparticles as highly active and reusable catalysts in the C1–C3 alcohol oxidation and the room temperature dehydrocoupling of dimethylamine-borane (DMAB), *J. Clust. Sci.* 27 (2016) 9; (b) F. Sen, G. Gokagac, Pt nanoparticles synthesized with new surfactants: improvement in C1–C3 alcohol oxidation catalytic activity, *J. Appl. Electrochem.* 44 (2014) 199; (c) F. Sen, Y. Karatas, M. Gulcan, N. Zahmakiran, Amylamine stabilized platinum(0) nanoparticles: active and reusable nanocatalyst in the room temperature dehydrogenation of dimethylamine-borane, *RSC Adv.* 4 (2014) 1526–1531.
- [33] X. Huang, X. Qi, F. Boey, H. Zhang, Graphene-based composites, *Chem. Soc. Rev.* 41 (2012) 666–686.
- [34] W.Z. Li, W.J. Zhou, H.Q. Li, Z.H. Zhou, B. Zhou, G.Q. Sun, Q. Xin, Nanostructured Pt-Fe/C as cathode catalyst in direct methanol fuel cell, *Electrochim. Acta* 49 (2004) 1045.
- [35] S.L. Knupp, W.Z. Li, O. Paschos, T.M. Murray, J. Snyder, P. Haldar, The effect of experimental parameters on the synthesis of carbon nanotube/nanofiber supported platinum by polyol process-ing techniques, *Carbon* 46 (2008) 1276.
- [36] F. Colmati, E. Antolini, E.R. Gonzalez, Pt-Sn/C electrocatalysts for methanol oxidation synthesized by reduction with formic acid, *Electrochim. Acta* 50 (2005) 5496–5503.

- [37] K. Eid, H. Wang, V. Malgras, Z.A. Allothman, Y. Yamauchi, L. Wang, Facile synthesis of porous dendritic bimetallic platinum-nickel nanocrystals as efficient catalysts for the oxygen reduction reaction, *Chem. Asian J.* 11 (9) (2016) 1388–1393, <http://dx.doi.org/10.1002/asia.201600055>.
- [38] M. Pramanik, C. Li, Y.V. Kanetia, Y. Yamauchi, A mesoporous tin phosphate-graphene oxide hybrid toward the oxygen reduction reaction, *Chem. Commun.* 53 (2017) 5721.
- [39] H. Wang, J. Du, Z. Yao, R. Yue, C. Zhai, F. Jiang, Y. Du, C. Wang, P. Yang, Facile fabrication, characterization of Pt-Ru nanoparticles modified reduced graphene oxide and its high electrocatalytic activity for methanol electrooxidation, *Colloids Surf. A* 436 (2013) 57–61.
- [40] Z. Li, L. Zhang, X. Huang, L. Ye, S. Lin, Shape-controlled synthesis of Pt nanoparticles via integration of graphene and β -cyclodextrin and using as a novel electrocatalyst for methanol oxidation, *Electrochim. Acta* 121 (2014) 215–222.
- [41] Y. Hu, P. Wu, H. Zhang, C. Cai, Synthesis of graphene-supported hollow Pt-Ni nanocatalysts for highly active electrocatalysis toward the methanol oxidation reaction, *Electrochim. Acta* 85 (2012) 314–321.
- [42] S. Lin, C. Shen, D. Lu, C. Wang, H. Gao, Synthesis of Pt nanoparticles anchored on graphene-encapsulated Fe_3O_4 magnetic nanospheres and their use as catalysts for methanol oxidation, *Carbon* 53 (2013) 112–119.
- [43] C. Young, R.R. Salunkhe, S.M. Alshehri, T. Ahamad, Z. Huang, J. Henzie, Y. Yamauchi, High energy density supercapacitors composed of nickel cobalt oxide nanosheets on nanoporous carbon nanoarchitectures, *J. Mater. Chem. A* 5 (2017) 11834–11839, <http://dx.doi.org/10.1039/c7ta01362k>.
- [44] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, *Phys. Rep.* 473 (2009) 51–87.
- [45] M.S. Dresselhaus, A. Jorio, R. Saito, Characterizing graphene, graphite, and carbon nanotubes by raman spectroscopy, *Annu. Rev. Condens. Matter Phys.* 1 (2010) 89–108.
- [46] D. Chen, Y. Zhao, Y. Fan, W. Wang, X. Li, X. Peng, X. Wang, J. Tian, Preparation and characterization of core-shell-like PbPt nanoparticles electro-catalyst supported on graphene for methanol oxidation, *Int. J. Hydrogen Energy* 39 (2013) 16053–16060.
- [47] S. Yu, Q. Liu, W. Yang, K. Han, Z. Wang, H. Zhu, Graphene- CeO_2 hybrid support for Pt nanoparticles as potential electrocatalyst for direct methanol fuel cells, *Electrochim. Acta* 94 (2013) 245–251.

Update

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Corrigendum

Corrigendum to “Enhanced electrocatalytic activity and durability of Pt nanoparticles decorated on GO-PVP hybri

nanoparticles decorated on GO-PVP hybri

material for methanol

oxidation reaction” [Appl. Catal., B 219 (2017) 511–516]

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The authors regret that Figs. 1 and 2b have been published erroneously. Therefore, the authors would like to replace it with the correct one given below. In current version, the mean particle size of prepared nanoparticle is about 3.94 nm as shown in TEM image. This does not alter the discussion. The authors confirm that this change does not affect the originality and importance of the scientific findings reported in the paper. The authors would like to apologise for any inconvenience caused.

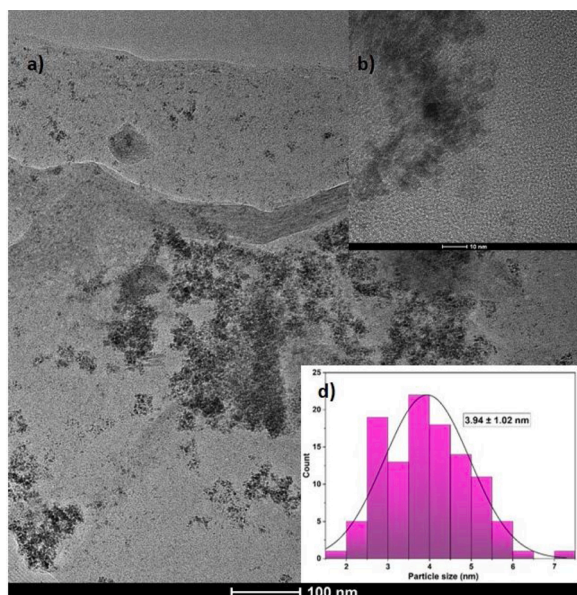


Fig. 1. TEM image (a), HRTEM image (b) and the particle size histogram (d) of Pt@GO-PVP NPs.

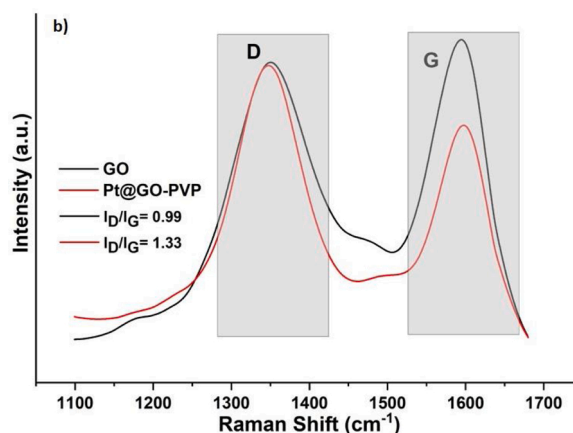


Fig. 2. (b) Raman spectra of GO and Pt@GO-PVP.

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